Quantum cascade laser measurements of stratospheric methane (CH_4) and nitrous oxide (N_2O)

Christopher R. Webster, Gregory J. Flesch, David C. Scott, James Swanson, Randy D. May, and W. Steven Woodward
Jet Propulsion Laboratory, California Institute of Technology

Claire Gmachl, Federico Capasso, Deborah L. Sivco, James N. Baillargeon, Albert L. Hutchinson, Alfred Y. Cho
Lucent Technologies, Bell Laboratories

Abstract

A tunable Quantum-Cascade (QC) laser has been flown on NASA's ER-2 high-altitude aircraft to produce the first atmospheric gas measurements using this newly-invented device, an important milestone in the QC laser's much-anticipated future planetary, industrial, and commercial application. From three aircraft flights in September 1999, measurements of methane (CH_4) and nitrous oxide (N_2O) gas were made from the ground to 70,000 ft in the stratosphere over the northern United States as part of a NASA tracer gas intercomparison mission. The QC laser operating near 8 μm wavelength was produced by the groups of Federico Capasso and Alfred Cho of Bell Labs, Lucent Technologies, where QC lasers were invented in 1994. Following spectral characterization and testing, the device was integrated into the Aircraft Laser Infrared Absorption Spectrometer (ALIAS) by Chris Webster's JPL group who made the measurements. The QC laser worked extremely well during the aircraft mission. Compared to its companion lead-salt tunable diode lasers (TDL) in the other three channels that showed laser linewidths of 50-100 MHz, the QC laser linewidth was measured to be only 17 MHz, this parameter being limited by current drive fluctuations. Furthermore, while the lead-salt TDL devices put out only ~0.1 mW output power with mode purities varying from 75 to 96%, the QC laser delivered about 10 mW of output power with a constant 96% single mode purity. The sensitivity of the QC laser channel was estimated from the background noise level of the spectra. For a 2-minute average, a minimum-detectable absorptance of only $\sim 5 \times 10^{-5}$ was observed, corresponding to a minimum-detectable mixing ratio for methane of about 2 ppbv. The QC laser measurements demonstrated several practical advantages over the traditional lead-salt devices, in addition to higher output power and single mode purity. The stratospheric flights reported here represent an important milestone in demonstrating the application of QC lasers to Earth and planetary atmospheric measurements. In addition to numerous industrial and commercial applications, the development of room-temperature QC lasers will undoubtedly have an enormous impact on our ability to produce miniaturized spectrometers that perform highly-sensitive *in situ* identification and quantitative characterization of Earth and planetary atmospheres, aerosols, and their surface and sub-surface mineralogy.

1. Introduction

1.1 In situ laser spectrometers for Earth and planetary measurements

Both Earth and planetary atmospheric science has long-awaited the development of single-mode tunable laser sources that operate in the mid-IR region at room temperatures. For over a decade, tunable laser sources in this wavelength region have relied upon lead-salt tunable diode lasers (TDLs), which have required cooling typically to 80 K or below, using liquid cryogens, J-T or Sterling cycle coolers[1]. Except for limited duration applications (e.g. descending probe measuring vertical profiles[2] needing only a few hours of operation), this approach is not practical for longer duration missions, and has inhibited the miniaturization of the spectrometers. Lead-salt TDLs suffer also from spectral degradation and reliability issues associated with thermal re-cycling.

For most planetary applications, whether a rover, lander, aerobot, or descending sub-surface probe, severe power, mass, and volume limitations apply. For this reason, difference frequency generation from various mixing schemes (e.g. two different wavelength near-IR TDLs) is possible[3], but ideally, single device tunable laser sources are needed. Progress in raising the operating temperature of lead-salt TDL devices to room temperature has been painfully slow[1], and has not been achieved in two decades of development. The disappointment in the lead-salt TDL development has been partially replaced by the development of room-temperature near-IR diode lasers in the 1-2-μm region[4]. These devices have had a large impact on Mars experiments, where H_2O and CO_2 are present in sufficient quantity to offset the weakness of absorption in this near-IR region. Room-temperature (TE cooler) tunable diode laser (TDL) sources of high spectral purity (single mode) and high output powers (5-50 mW) are now available in the near-IR region where molecules like H_2O and CO_2 have sufficiently strong IR absorption cross-sections. For other gas-phase species, systems with increased optical pathlengths offer a means of offsetting the loss in molecular absorption cross-sections. However, increasing pathlengths by factors of 100 is not usually compatible with miniaturization efforts, and not possible in applications with restricted space (e.g. sub-surface probe). For wavelengths in the 1-2 μm-range, JPL's MicroDevices Lab (MDL) have produced single-mode Distributed FeedBack (DFB) devices which have been tested and integrated into the Mars MVACS lander payload of the Mars 98 Surveyor mission: one for measurement of atmospheric H_2O at 1.37 μm and isotopic CO_2 at 2.04 μm (TDL Met)[5]; and a second as an analyzer for evolved H_2O and CO_2 from heated soil (TEGA)[5].

Tunable lasers operating near room-temperature would promise a new generation of miniature tunable laser mid-IR spectrometers for *in situ* measurement of atmospheric and evolved planetary gases. Such an all-solid-state spectrometer would have immediate applications to Mars, Titan, Venus and Europa missions, could be operated on a descending or penetrating probe, lander, rover, or aerobot, would consume only a few watts of power, and weigh less than one kilogram[6]. Because it directly accesses the wavelength region of strong vibration-rotation spectral lines, a mid-IR laser spectrometer has wide-ranging and immediate application to measuring concentrations of several planetary gases such as H_2O, CH_4, CO, CO_2, C_2H_2, HCN, C_2H_6, C_2N_2, HC_3N, O_3, OCS, H_2S, and SO_2, and numerous stable isotopes. Such measurements could be made to study (i) atmospheric photochemistry and transport of Mars, Titan[2], and Venus; (ii) Mars and Europa mineralogical and biological experiments (e.g. quantification of evolved gases and their isotopic fractionation from thermal decomposition of minerals or ice); and (iii) respiratory and hazardous gas monitoring for human exploration of the solar system.

1.2 The quantum-cascade (QC) laser

A huge leap in laser technology has been made in the last few years by Federico Capasso and Alfred Cho's groups at Bell Laboratories, Lucent Technologies, with the invention of the quantum-cascade (QC) laser[7,8,9]. This device, available pulsed at room-temperature operation and cw at lower temperature operation, produces tunable mid-IR laser output from a revolutionary new approach to laser design, that of quantum engineering of electronic energy levels. Quantum-cascade lasers are fundamentally different from diode lasers in that the wavelength is essentially determined by quantum confinement, i.e. by the thickness of active layers rather than the energy bandgap of the material. By tailoring the active layer thickness, the laser wavelength can be selected over a wide range (3-12 μm) of the IR spectrum using the same material[7,8,9]. In addition QC lasers have much higher power than diode lasers at the same wavelength because an electron after emitting a laser photon in the first active region stage of the device is recycled and reinjected into the following stage where it emits another photon. A typical QC laser has $N = 25 - 75$ stages so that N laser photons are emitted per injected electron. These new devices produce single-mode laser light tunable over 10-20 cm^{-1}, of output power (fractions of a watt) hundreds of times greater than that of lead-salt lasers at cryogenic temperatures. Furthermore, these devices are highly reliable, with long-duration spectral integrity. The technological breakthrough provided by the invention of the QC laser offers a ten-fold increase in our current ability to address science objectives for Earth and planetary missions.

Progress in QC laser development has been very rapid. Room temperature (300 K) operation has been demonstrated in pulsed operation from 3.6 to 11.5 μm, with extremely high output peak powers up to half a Watt[10,11]. In the wavelength region of 5 - 8 μm, cw operation at temperatures above 120 K produces output power levels of 2-20 mW, and about 200 mW at 80 K[11]. Note that cw Pb-salt TDLs produce only 0.2 mW at 80 K[1].

For high-resolution spectroscopic applications, single mode operation with narrow linewidth and high tunability is required. Recently, the distributed-feedback (DFB) principle was applied to QC lasers . A single-mode tuning range of 100 nm was demonstrated with a tuning coefficient of 0.35 nm/K at 5.2 μm, and 0.55 nm/K near 8 μm[11]. To date, QC-DFB lasers have been fabricated at various wavelengths from 5-11.5 μm. QC-DFB lasers have been used in the laboratory to demonstrate detection of N_2O at 7.8 μm close to room temperature. In the very first spectroscopic measurements made with a room temperature QC-DFB laser, Namjou and coworkers[12] used wavelength modulation to detect both N_2O and CH_4 near 8 μm. Sensitivities achieved were equivalent to minimum detectable absorptances of 5 parts in 10^5, within a factor of ten of that demonstrated for TDL measurements[13].

Continuous-wave (cw) operation of tunable lasers offers the most sensitive means of gas detection, since cw devices are associated with very small laser linewidths (typically tens of MHz) and phase-sensitive detection may be employed. Although QC-DFB lasers operate cw at 80 K with fractions of a watt of output power, room temperature operation is only currently achieved in a pulsed mode. In the pulsed configuration, QC-DFB lasers are driven with pulses of about 10 ns duration, with up to 1 MHz repetition rates. Despite the low duty-cycle of about 1%, the average laser powers demonstrated using room temperature pulsed QC-DFB lasers (>10 μW) is still high enough to compete favorably with even cooled lead-salt devices, that produce typically 100 μW cw single-mode. Laser linewidth is of more concern. Namjou and coworkers[12] measured a laser linewidth of 720 MHz, compared to typical molecular linewidths (HWHM at 6-8 μm) of about 50 MHz (0.0017 cm^{-1}) at very low pressures (Doppler-broadened), and about 3,000 MHz (0.1 cm^{-1}) at atmospheric pressure. More recently, kilohertz-level linewidths have been measured[14] from frequency-stabilized cw DFB QC lasers, and spectroscopic measurements have included Doppler-limited[15] and photoacoustic[16] spectroscopy.

2. *Stratospheric measurements from the ER-2 aircraft*

Over the past 16 years, Webster's JPL group has pioneered the development of tunable laser spectrometers for Earth and planetary applications. Currently, the group has nine laser spectrometers for aircraft, balloon, and spacecraft, including two on the Mars lander payload preparing for landing on Mars this December. In over 250 aircraft and balloon flights, the group has demonstrated the high sensitivity of tunable laser absorption spectroscopy for *in situ* measurement of atmospheric gas concentrations in the mid-IR (3-8 μm) region, including tracers like N_2O CO, H_2O, and CH_4, radicals like NO, NO_2, and reservoir gases like HCl and HNO_3 [2,5,17,18,19].

In preparation for a series of aircraft flights over Sweden in spring 2000 as part of NASA's SAGE III Ozone Loss and Validation Experiment (SOLVE) mission, JPL's Aircraft Laser Infrared Absorption Spectrometer (ALIAS)[18] was taken to Edwards Air Force Base in September for test flights on NASA's ER-2 aircraft. The ER-2 aircraft is a single-engine, high-altitude aircraft that is a modified U2 aircraft, capable of flying to altitudes greater than 80,000 ft. On September 23, 25, and 28, 1999, NASA pilots Ken Broida, Jan Nystrom, and Jim Barrilleaux each flew a single flight out of NASA Dryden/ Edwards Air Force Base on 2-8 hour sorties that made up a science measurement intercomparison series. With four-laser capability in the liquid nitrogen dewar of the ALIAS instrument, a QC laser operating near 8 μm wavelength (1261 cm^{-1}) had been incorporated to measure the gases nitrous oxide (N_2O) and methane (CH_4).

The QC laser worked extremely well during the aircraft mission. Compared to its companion lead-salt diode lasers in the other three channels that showed laser linewidths of 50-100 MHz, the QC laser linewidth was measured to be only 17 MHz, this parameter being limited by current drive fluctuations. Furthermore, while the lead-salt devices put out only 0.1 mW output power with mode purities varying from 75 to 96%, the QC laser delivered about 10 mW of output power with a constant 96% single mode purity. The QC laser demonstrated several practical advantages of the traditional lead-salt devices, in addition to higher output power and single mode purity.

First of all, the device was recycled numerous times without performance degradation. Secondly, the QC laser exhibited very slow tuning with temperature and current that proved to be a blessing in the flight. The slow current tuning rate (~115 MHz/mA, which is about 10 times less than typical Pb-salt TDLs) means that the current noise contribution is smaller, producing narrower laser linewidths. More important, the slower temperature tuning (~ 0.1 cm^{-1}/degree K) made the selected scan range much less dependent on changes in the exact cold finger temperature. During the flight of September 28, a heater failure near the end of flight caused O-rings in the dewar seal to partially fail, causing the spectral lines from all three lead-salt laser channels to move quickly off screen as the loss of pressure warmed the cold -finger by a few degrees. The QC laser spectral scan, however, barely moved, because it was so much less sensitive to the cryogen temperature, so that its scan of N_2O and CH_4 lines remained on-screen the whole flight. Like all data recording on ALIAS, spectra and therefore gas measurements are made every one second. The sensitivity of the QC laser channel may be estimated from the background noise level of the spectra. For a 2-minute average, a minimum-detectable absorptance of only ~5 x 10^{-5} was observed, corresponding to a minimum-detectable mixing ratio for methane of about 2 ppbv.

Historically, both methane and nitrous oxide have been used as important long-lived tracers of large-scale atmospheric circulation. They are both produced at the Earth's surface and photochemically removed in the stratosphere. *In situ* observations of N_2O and CH_4 show distinct compact relationships for the tropics and extra-tropics[20]. The variation of their vertical profiles with latitude has been used to infer processes that entrain mid-latitude air into the tropics [21]. Although by themselves the stratospheric measurements made here do not reveal new insights into these processes, they are nevertheless fully consistent with these earlier studies.

Under collaboration with the groups at Bell Labs, the JPL group is currently building a prototype QC laser spectrometer that may fly on the payload of NASA's Mars Airplane[6], currently under review for a 2003 landing on Mars to celebrate the 100 year anniversary of the Wright brothers' historic flight. The prototype QC-laser spectrometer would be a 4-laser miniature spectrometer operating at room temperature, and using HgCdZnTe detectors. The whole instrument will weigh less than 1 lb., and have capability for 6 gas species measurements at the ppb-level. QC lasers on board would make measurements of biogenic and geothermal gases like methane and sulfur dioxide that may be present in the Martian atmosphere.

Acknowledgements:
Part of the research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration. Funding from NASA's Upper Atmospheric Research Program (UARP) and Planetary Instrument Definition and Development Program

(PIDDP) is gratefully acknowledged. The aircraft flights were made as part of UARP's Sage III Ozone Loss Validation Experiment (SOLVE) mission. The work done at Bell Laboratories is supported in part by DARPA/US Army Research Office under Contract No. DAAG55-98-C-0050.

References:

1. M. Tacke, "New developments and applications of tunable IR lead salt lasers", *Infrared Phys. Technol.*, ***36***, 447-463, 1995.
2. "Tunable Diode Laser Infrared Spectrometer for In-situ Measurements of the Gas Phase Composition and Particle Size Distribution of Titan's Atmosphere", C.R. Webster, S.P. Sander, R. Beer, R.D. May, R.G. Knollenberg, D.M. Hunten, and J. Ballard, *Appl. Opt.* ***29***, 907-917, (1990).
3. K.P. Petrov, A.T. Ryan, T.L. Patterson, L. Huang, and S.J. Field, "Mid-IR spectroscopic detection of trace gases using guided-wave difference-frequency generation", *Appl. Phys. B*, ***67***, 357-351, 1998.
4. S. Forouhar, S. Keo, A. Larsson, A. Ksendzov, and H. Temkin, "Low-threshold continuous operation of InGaAs/InGaAsP quantum well lasers at 2 microns", *Electron. Lett.*, ***29***, 574-576, 1993.
5. R. D. May, S. Forouhar, D. Crisp, W.S. Woodward, D.A. Paige, A. Pathare, and W.S. Boynton, "The MVACS tunable diode laser spectrometers", submitted *to J. Geophys. Res.*, special issue on Mars98, 1999.
6. C.R. Webster, "Quantum cascade laser spectrometer for in situ atmospheric and evolved gases on Mars, Titan, Venus, and Europa", *NASA Tech Brief*, 1999.
7. J. Faist, F. Capasso, D. L. Sivco, C. Sirtori, A. L. Hutchinson, and A. Y. Cho, "Quantum Casacde Laser", *Science* ***264***, 553 (1994);
8. F. Capasso, C. Gmachl, D. L. Sivco, and A. Y. Cho, "Quantum cascade lasers" *Physics World* ***12,*** 27 - 33, June 1999.
9. F. Capasso, C. Gmachl, A. Tredicucci, D. L. Sivco, A. L. Hutchinson, and A. Y. Cho, "Quantum cascade lasers", *Optics and Photonics News,* ***10 (10),*** *31 - 37*, 1999.
10. C. Gmachl, J. Faist, J. N. Baillargeon, F. Capasso, C. Sirtori, D. L. Sivco, S. N. G. Chu, and A. Y. Cho, "Complex-Coupled Quantum Cascade Distributed-Feedback Laser", *IEEE Photon. Technol. Lett.* ***9***, 1090 - 1092, 1997.
11. C. Gmachl, F. Capasso, J. Faist, A. L. Hutchinson, A. Tredicucci, D. L. Sivco, J. N. Baillargeon, S. N. G. Chu, and A. Y. Cho, "Continuous-wave and high-power pulsed operation of index-coupled distributed feedback quantum cascade laser at $\lambda \approx 8.5$ μm", *Appl. Phys. Lett.* ***72***, 1430-1432 (1998).
12. K. Namjou, S. Cai, and E. A. Whittaker, J. Faist, C. Gmachl, F. Capasso, D. L. Sivco, and A. Y. Cho, "Sensitive absorption spectroscopy with a room-temperature distributed-feedback quantum-cascade laser", *Opt. Lett.* ***23***, 219 - 221, 1998.
13. R.D. May and C.R. Webster, "Balloon-borne Laser Spectrometer Measurements of NO_2 with Gas Absorption Sensitivities Below 10^{-5}", *Appl. Opt.* ***29***, 5042-5044, (1990).

14. R. M. Williams, J. F. Kelly, J. S. Hartman, S. W. Sharpe, M. S. Taubman, J. L. Hall, F. Capasso, C. Gmachl, D. L. Sivco, J. N. Baillargeon, and A. Y. Cho, "Kilo-Hertz Linewidth from Frequency Stabilized Mid-Infrared Quantum Cascade Lasers", *Opt. Lett., in press* 1999.
15. S. W. Sharpe, J. F. Kelly, J. S. Hartman, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, and A. Y. Cho, "High-resolution (Doppler-limited) spectroscopy using quantum-cascade distributed feedback lasers", *Opt. Lett.* ***23***, 1396 - 1398, 1998.
16. B. A. Paldus, T. G. Spence, R. N. Zare; J. Oomens, F. M. J. Harren, D. H. Parker; C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, and A. Y. Cho, "Photoacoustic spectroscopy using quantum-cascade lasers", *Opt. Lett.* ***24***, 178 - 180 (1999).
17. C. R. Webster, R. D. May, R. Toumi, and J. Pyle, "Active Nitrogen Partitioning and the Nighttime Formation of N_2O_5 in the Stratosphere: Simultaneous In-situ Measurements of NO, NO_2, HNO_3, O_3, N_2O, and jNO_2 Using the BLISS Diode Laser Spectrometer", *J. Geophys. Res.* ***95,*** 13,851-13,866, (1990).
18. "Aircraft (ER-2) Laser Infrared Absorption Spectrometer (ALIAS) for In-situ Stratospheric Measurements of HCl, N_2O, CH_4, NO_2, and HNO_3", C.R. Webster, R.D. May, C.A. Trimble, R.G. Chave and J. Kendall, *Applied Optics*, ***33***, 454-472, 1994.
19. "Airborne Laser Infrared Absorption Spectrometer (ALIAS-II) for *In situ* Atmospheric Measurements of N_2O, CH_4, CO, HCl, and NO_2 from Balloon or RPA Platforms" D.C. Scott, R.L. Herman, C.R. Webster, R.D. May, G.J. Flesch, and E.J. Moyer, *Applied Optics,* ***38***, 4609-4622, 1999.
20. "Tropical entrainment timescales inferred from stratospheric N_2O and CH_4 observations", R.L. Herman, D.C. Scott, C.R. Webster, R.D. May, E.J. Moyer, R.J. Salawitch, Y.L. Yung, G.C. Toon, B. Sen, J.J. Margitan, K.H. Rosenlof, H.A. Michelsen, J.W. Elkins, *Geophys. Res. Letters*, ***25***, 2781-2784, 1998.

FIGURE CAPTIONS

Figure 1

Schematic of the geometry of a quantum-cascade laser package.

Figure 2

Four QC lasers are mounted onto a gold-coated oxygen-free copper heat sink designed for compatibility with typical lead-salt TDL packages. Only two lasers are wire-bonded to connections for use (one as an unused spare).

Figure 3

NASA's ER-2 high-altitude aircraft takes off from Dryden Flight Research Center (NASA photo courtesy Tony Landis). The ALIAS laser spectrometer is located in the superpod seen on the right wing. This payload carries numerous other NASA, NOAA and university experiments.

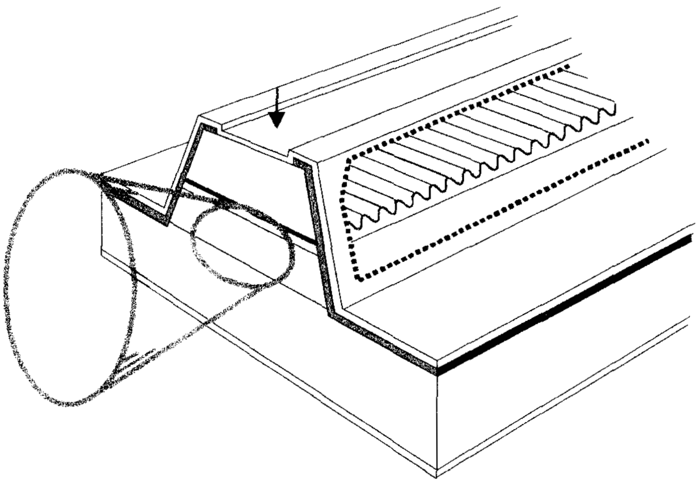
Figure 4

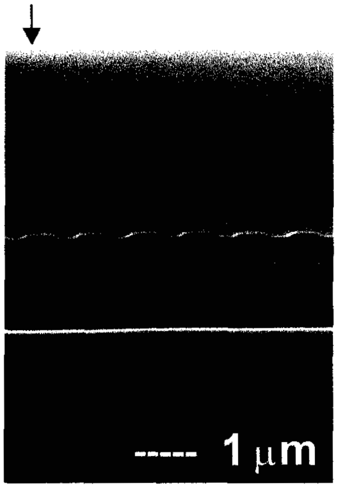
QC laser spectral scans of reference gas cell, Ge etalon with free-spectral-range of 0.015 cm^{-1}, and actual flight spectrum showing second-harmonic lineshapes from CH_4 and N_2O. Four spectra like this one are recorded in flight every one second.

Figure 5

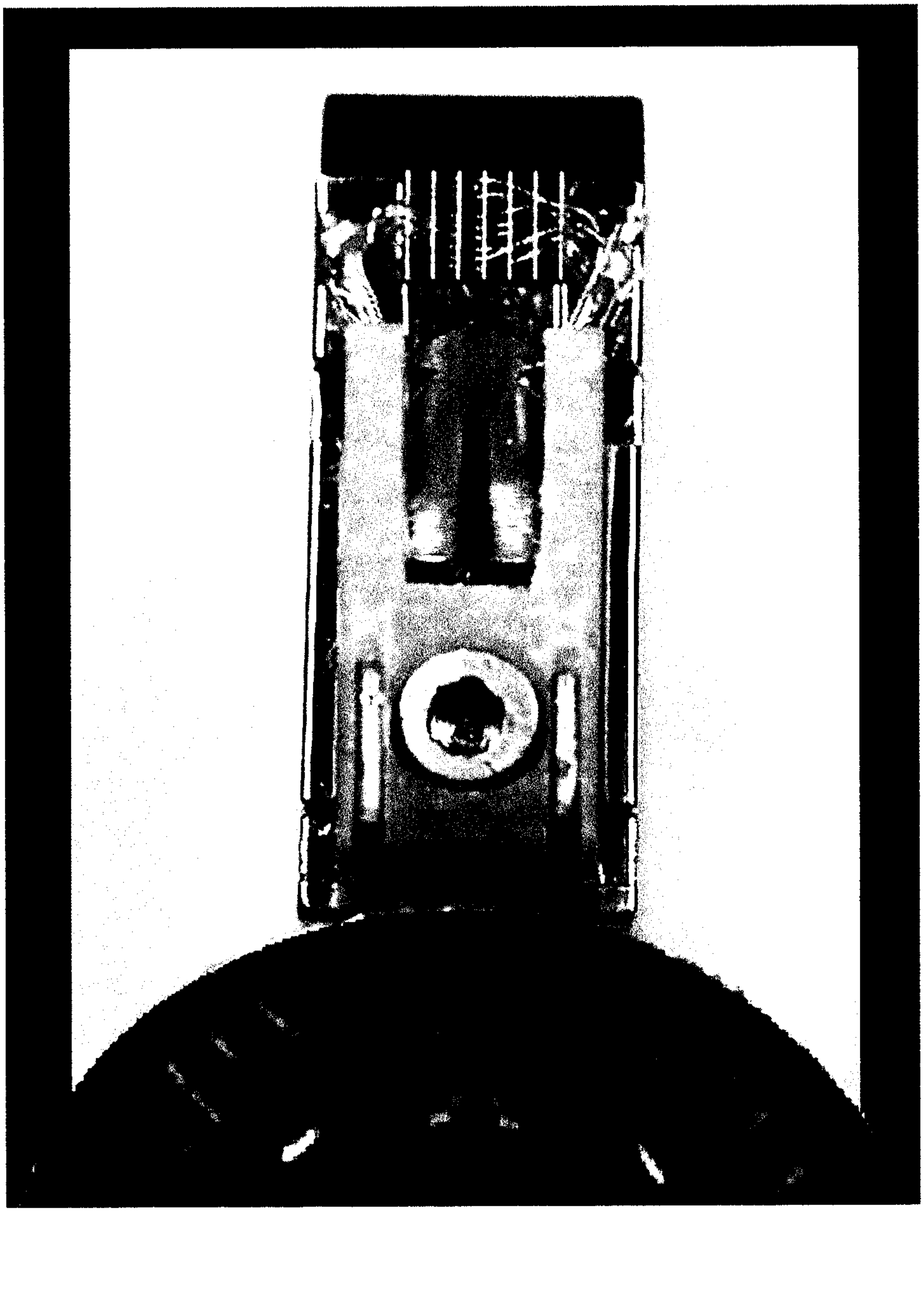
Final one-second flight data for CH_4 measurements during the ascent for the flight of 990928. The QC laser results compare very favorably with those of the traditional Pb-salt TDL's. Lower volume mixing ratios of CH_4 generally are associated with higher altitudes.

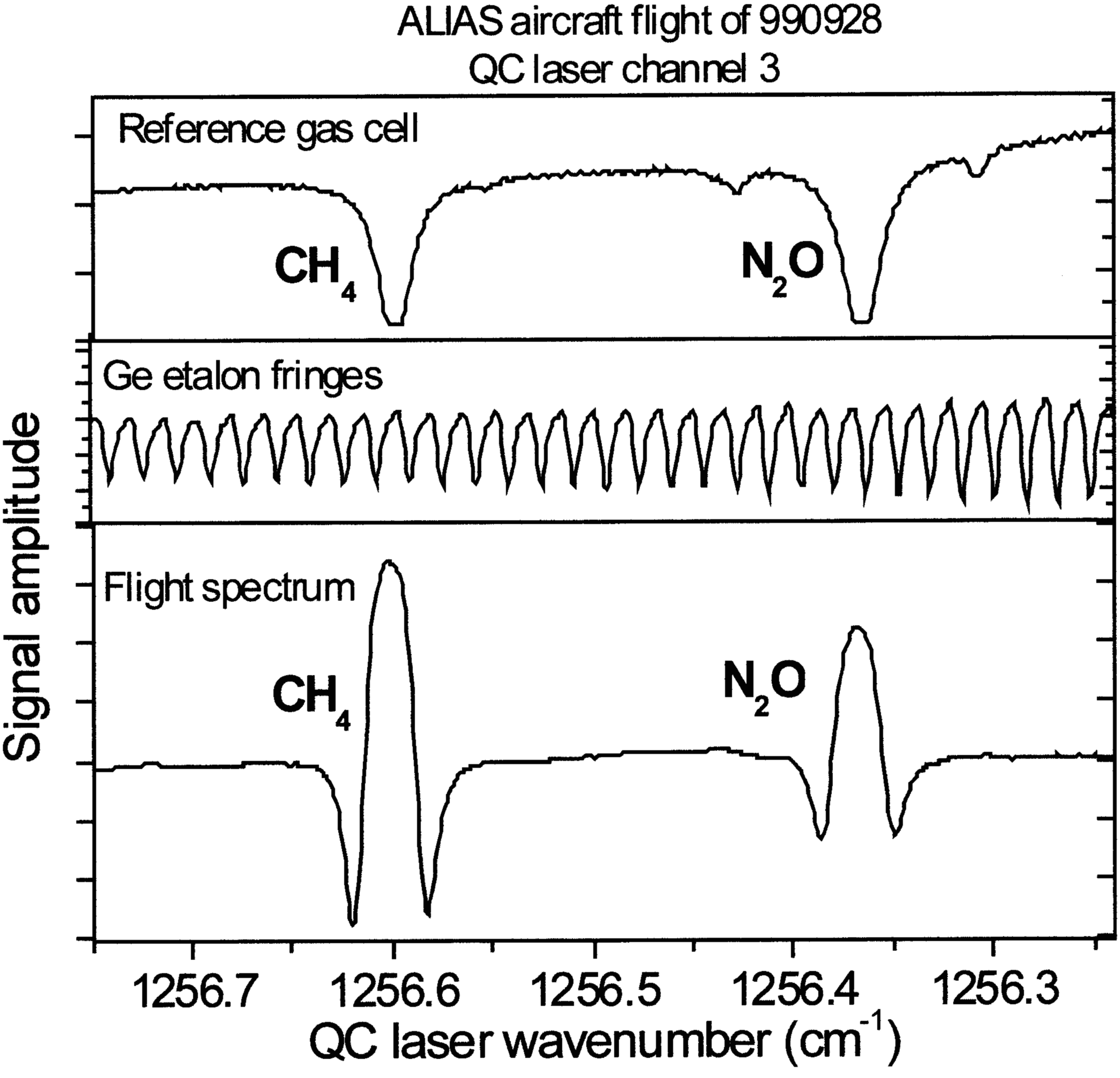
QC - distributed feedback laser

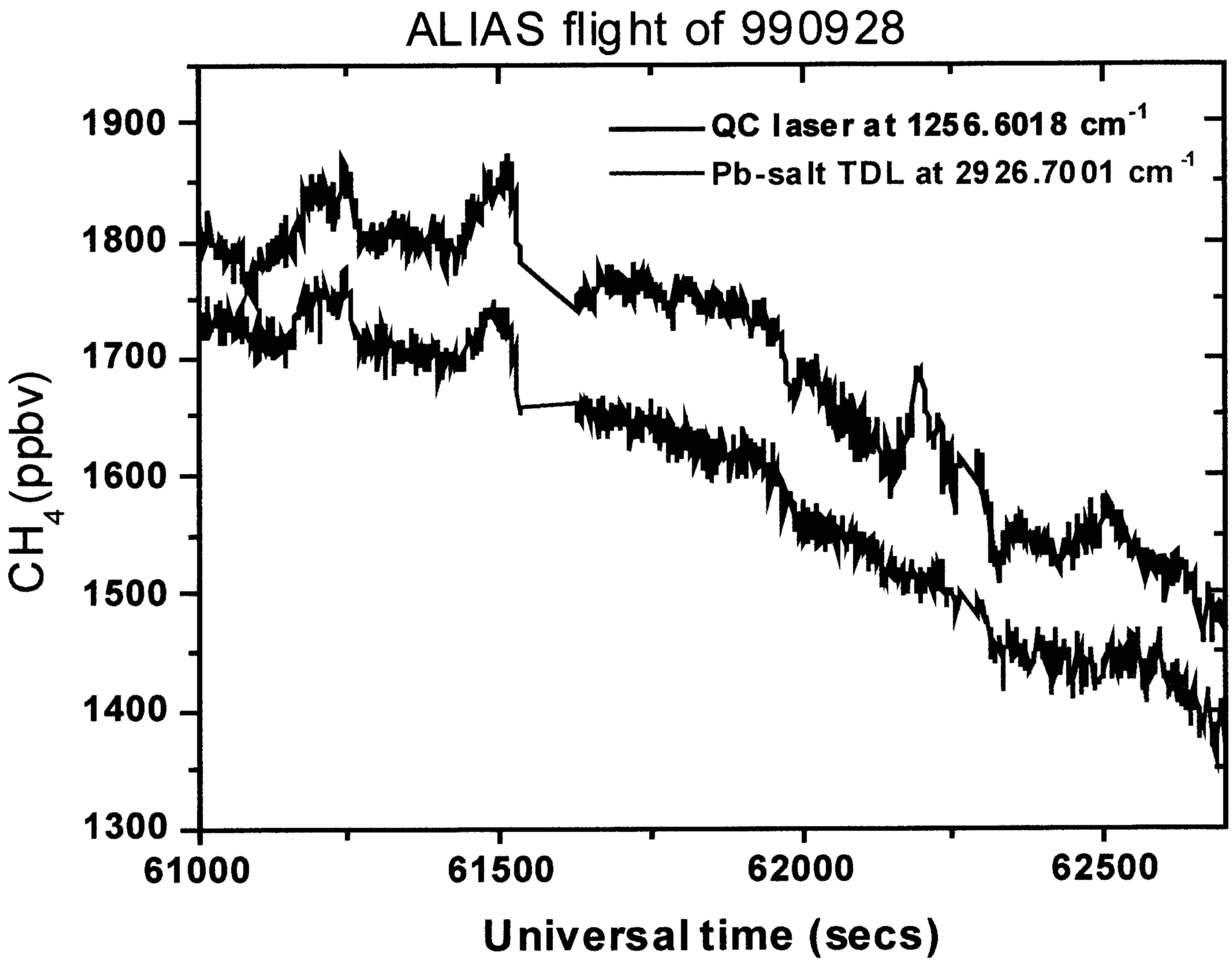




can cover entire mid-infrared wavelength range




ALIAS aircraft flight of 990928
QC laser channel 3
Reference gas cell
CH4
N2O
Ge etalon fringes
Flight spectrum
CH4
N2O
Signal amplitude
1256.7
1256.6
1256.5
1256.4
1256.3
QC laser wavenumber (cm-1)


ALIAS flight of 990928
QC laser at 1256.6018 cm-1
Pb-salt TDL at 2926.7001 cm-1
1900
1800
1700
1600
1500
1400
1300
CH4 (ppbv)
61000
61500
62000
62500
Universal time (secs)